

product from the pinacol coupling of 4-*tert*-butylcyclohexanone.³³

Reaction of *tert*-Butyl Hypochlorite with *syn*-, *anti*-, and *syn/anti*- (1:1) 4,4'-Di-*tert*-butylcyclohexylidene-cyclohexane. To a stirred solution of 272 mg of *syn* olefin in 1.5 mL of C₆D₆ was added 110 mg of *tert*-butyl hypochlorite in 0.5 mL of C₆H₆. The reaction mixture was stirred at room temperature for 1 h. ¹H NMR indicated a total conversion of the olefin to the two 1-(4-*tert*-butyl-1-cyclohex-1-enyl)-4-*tert*-butyl-1-chloro-cyclohexane in the ratio 2:1. The ¹H NMR spectrum is almost identical with the ¹H NMR spectrum of the corresponding hydroxy compounds, obtained by NaBH₄ reduction of the hydro-

peroxide. The latter was obtained via ¹O₂ oxygenation of the *syn* or *anti* olefin. Standing at room temperature in C₆D₆, both allylic chlorides afforded the diene within several hours. The ¹H NMR (C₆D₆) data of the two allylic chlorides are as follows: δ 6.05–5.7 (br, 1 H), 2.7–1.3 (br, 14 H), 0.98 (s), 0.92 (s), 0.89 (s), 0.83 (s); the last four signals were integrated for 18 H and have a ratio 2:2:1:1, as well for the *syn*, *anti*, and *syn/anti* (1:1) compounds.

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(33) Asveld, E. W. H. Dissertation, Groningen, 1980.

Thermal Decomposition of Some Perfluoro- and Polyfluorodiacyl Peroxides

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Seven polyfluoroacyl peroxides were synthesized, some of them by a new procedure involving the direct interaction of an acyl fluoride with hydrogen peroxide. In the temperature range of 20–40 °C, all these peroxides undergo first-order decomposition in dilute 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) solutions (≤0.02 M.). The major decomposition products were separated and characterized as the coupling products of the corresponding radicals, R_F·-R_F·. Differing from other perfluoro or polyfluoro radicals, the perfluoro- α -isopropoxyethyl radicals (10) undergo substantial β scission to form perfluoroisopropyl radicals (11) during their lifetime. The ΔH^\ddagger values for the perfluoroacyl peroxides are about 24 kcal mol⁻¹, or about 5 kcal lower than that of the nonfluorinated diacyl peroxides (~29 kcal mol⁻¹). Apparently, the higher relative rates for 3 and 7 are caused by different factors. The latter peroxide (7) decomposes with a more favorable ΔS^\ddagger term, whereas the former (3) decomposes with lower values of both ΔH^\ddagger and ΔS^\ddagger . Thus, weakening of the peroxide bond by H bonding of the peroxide oxygen atom with the acidic ω -hydrogen atom seems to be implicated in the decomposition of 3. With a half-life of 81 min at 20 °C, 3 may become a useful low-temperature initiator for free-radical reactions and polymerization.

Both theoretical and practical interests have unceasingly kept the research on diacyl peroxides active for many years. One important theoretical theme has been the mechanistic pathways of their decomposition, whether ionic or free radical or whether concerted or stepwise, in cases where homolysis pertains. Other aspects of interests concern themselves with structural and environmental effects on the rates and mechanistic paths of decomposition. The subject has been comprehensively reviewed by Hiatt² and Koenig,³ the impact of ESR and CIDNP on this branch of research is also well-known.^{4,5}

Most of all of the diacyl peroxides which had been investigated are hydrocarbon derivatives. Relatively few fluoro- or perfluorodiacyl peroxides are known, and available kinetic data are few.^{6,7} Since they have been

used as initiators for polymerization of fluoro olefins for years⁸ and they possess distinct structural characteristics, research on synthetic and mechanistic aspects of these compounds may yield useful information on both basic knowledge and practical applications.

Barium peroxide, sodium peroxide, and hydrogen peroxide have been used for the synthesis of perfluorodiacyl peroxides;^{10,11} the last two reagents were used in this work. In preparing peroxides by the reaction between aqueous sodium peroxide and perfluoroacyl chlorides, we made a preliminary study on the effects of various factors on the yields of the desired products. Among these factors, e.g., the reaction temperature, the amount of water, and the Na₂O₂/R_FCOCl molar ratio, the last one appeared rather important, and a value of 0.4–0.5 was preferred. When H₂O₂ was used in place of Na₂O₂, the procedure became even more convenient for the aqueous-organic two-phase system used. This procedure has been successfully adapted to the syntheses starting from acyl fluorides. All seven

(1) Formerly spelled Jiang Hsi-Kwei, Chiang Hsi-Kwei, or Stanley Hsi-Kwei Jiang (Chiang).

(2) R. Hiatt in "Organic Peroxides", Vol. 1, D. Swern, Ed., Wiley, New York, 1970, p 799.

(3) T. W. Koenig in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, 1973, p 113.

(4) J. K. Kochi in "Free Radicals", Vol. 2, J. K. Kochi, Ed., Wiley, New York, 1973, p 698.

(5) See, e.g., R. G. Lawler in "Chemically Induced Magnetic Polarization", L. T. Muus et al Eds., D. Reidel, Boston, 1977, p 17.

(6) Ronald A. DeMarco and Jeanne M. Shreeve, *Adv. Inorg. Chem. Radiochem.* 16, 109 (1974).

(7) V. A. Novikov, V. P. Sass, L. S. Ivanova, L. F. Sokolov, S. V. Sokolov, *Vysokomol. Soedin., Ser. A*, 17, 1235 (1975).

(8) (a) U.S. Patent 2700662 (1955); *Chem. Abstr.*, 49, 5886i (1955); (b) British Patent 781 532 (1958); *Chem. Abstr.*, 52, 1684c (1958); (c) U.S. Patent 2943 080 (1960); *Chem. Abstr.*, 54, 20399d (1960); (d) German Offen. 1 806 426 (1969); *Chem. Abstr.*, 71, 13533s (1969).

(9) B. C. Brodie, *J. Chem. Soc.*, 17, 266 (1864).

(10) C. C. Price and E. Krebs "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 649.

(11) P. E. Rice, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Sci.*, 12(1), 396 (1971).

Table I. Yields and Main Decomposition Products of Various Diacyl Peroxides

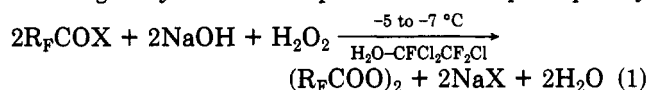
compd	$(R_F\text{COO})_2$	preparation		decomposition	
		starting matl	yield, %	main products	yield, %
1	$(n\text{-C}_3\text{F}_7\text{COO})_2$	$n\text{-C}_3\text{F}_7\text{COCl}$	69	$(n\text{-C}_3\text{F}_7)_2$	89
2	$(n\text{-C}_7\text{F}_{15}\text{COO})_2$	$n\text{-C}_7\text{F}_{15}\text{COCl}$	70	$(n\text{-C}_7\text{F}_{15})_2$	88
3	$(\text{HCF}_2\text{CF}_2\text{COO})_2$	$\text{HCF}_2\text{CF}_2\text{COCl}$	79	$(\text{HCF}_2\text{CF}_2)_2$	81
4	$[\text{H}(\text{CF}_2)_4\text{COO}]_2$	$\text{H}(\text{CF}_2)_4\text{COCl}$	70	$[\text{H}(\text{CF}_2)_4]_2$	62
5	$[\text{H}(\text{CF}_2)_6\text{COO}]_2$	$\text{H}(\text{CF}_2)_6\text{COCl}$	65	$[\text{H}(\text{CF}_2)_6]_2$	64
6	$[n\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COO}]_2$	$n\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COF}$	50	$[n\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)]_2$	65
7	$[i\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COO}]_2$	$i\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COF}$	60	$[i\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)]_2$	21
				$i\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}(\text{CF}_3)_2$	34
				$(i\text{-C}_3\text{F}_7)_2$	11

Table II. Kinetic Parameters for the Decomposition of the Perfluoro- and Polyfluorodiacyl Peroxides^a

compd	$(R_F\text{COO})_2$	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal deg ⁻¹	k_{rel}^b at 30 °C
1	$(n\text{-C}_3\text{F}_7\text{COO})_2$	23.9 ± 0.3	1.71 ± 0.4	1.00
2	$(n\text{-C}_7\text{F}_{15}\text{COO})_2$	23.4 ± 0.4	0.43 ± 1.2	1.31
3	$(\text{HCF}_2\text{CF}_2\text{COO})_2$	20.6 ± 0.3	-6.1 ± 1.0	4.85
4	$[\text{H}(\text{CF}_2)_4\text{COO}]_2$	24.0 ± 0.9	2.6 ± 1.4	1.49
5	$[\text{H}(\text{CF}_2)_6\text{COO}]_2$	24.0 ± 0.7	3.0 ± 1.0	1.35
6	$[n\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COO}]_2$	23.9 ± 0.1	3.3 ± 0.2	2.31
7	$[i\text{-C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COO}]_2$	24.5 ± 0.1	6.5 ± 0.2	4.06

^a Solvent Freon-113, initial concentration ≤ 0.02 M, temperature range 20–45 °C. ^b The rate of 1 at 30 ± 0.05 °C (8.50 × 10⁻⁵ s⁻¹) is taken as unity.

peroxides listed in Table I were prepared by this procedure, with the $R_F\text{COX}/\text{NaOH}/\text{H}_2\text{O}_2$ molar ratio being 1:1:0.5, according to eq 1. Excess amounts of aqueous NaOH would cause alkaline hydrolysis of $R_F\text{COX}$, thus reducing the yield. These peroxides decompose quickly



at room temperature and they are difficult to crystallize. Thus they were preserved as dilute solutions in Freon-113 at -78 °C. In order to obtain pure solutions, we used highly purified acyl halides as starting materials.¹² After the reaction, most of the unreacted acyl halides were washed away by aqueous NaHCO₃. It was experimentally shown that the small amounts of acyl halides which remained did not affect the rate of decomposition of the diacyl peroxides.

In order to avoid induced decomposition¹³ and heterolyses favored by polar solvents, the rates of decompositions of these diacyl peroxides were measured at very dilute initial concentrations (≤ 0.02 M) in a nonpolar solvent, Freon-113 (CF₂ClCFCl₂). Studies of the effect of concentration on the decomposition rate (e.g., see Table IV) show that induced decomposition is negligible at this concentration. Product analyses by mass and NMR spectra show that the main products are the coupling products $R_F\text{-}R_F$ expected from free-radical mechanisms;¹⁴ the results are also shown in Table I.

Rates of decomposition were measured in the 20–40 °C temperature range at 5 °C intervals, and the values are given in the Experimental Section. Results plotted in Figure 1 for the 30 °C runs show that all seven peroxides follow first-order kinetics in their decomposition; similar curves were obtained for other temperatures, and no indications of induced decomposition were observed.

The kinetic parameters for the thermal decomposition of the fluorodiacyl peroxides are listed in Table II, and the corresponding curves are shown in Figure 2. In Table III

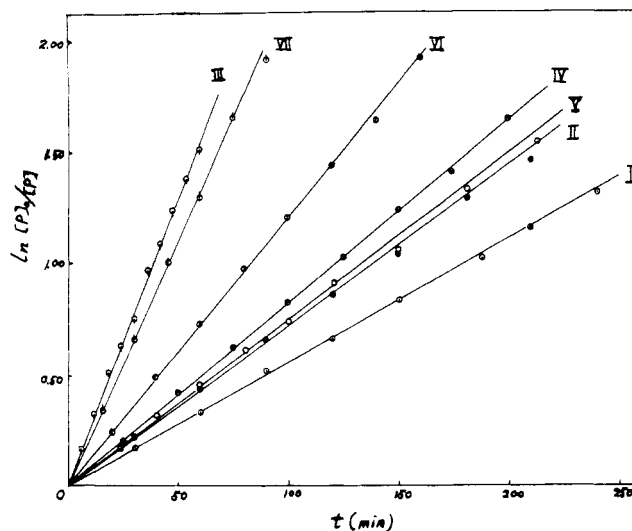


Figure 1. Thermal decomposition of perfluoro- and polyfluorodiacyl peroxide in Freon-113: initial concentration ≤ 0.02 M, temperature 30 ± 0.05 °C.

Table III. Kinetic Parameters for the Decomposition of Some Representative Hydrocarbon Diacyl Peroxides (RCOO)₂

R	solvent	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal deg ⁻¹
C_2H_5 ^a	$\text{C}_6\text{H}_5\text{CH}_3$	29.5	9.8
$n\text{-C}_3\text{H}_7$ ^a	$\text{C}_6\text{H}_5\text{CH}_3$	29.1	10.1
$n\text{-C}_4\text{H}_9$ ^a	$\text{C}_6\text{H}_5\text{CH}_3$	28.9	8.7
$n\text{-C}_5\text{H}_{13}$ ^a	$\text{C}_6\text{H}_5\text{CH}_3$	29.4	10.2
$n\text{-C}_6\text{H}_{15}$ ^a	$\text{C}_6\text{H}_5\text{CH}_3$	29.2	9.7
$i\text{-C}_3\text{H}_7$ ^b	isooctane	26.6	5.3
<i>trans</i> -4- <i>tert</i> -butylcyclohexyl ^b	CCl_4	19.5	-16.1

^a Calculated from the data of E. T. Denisov, "Liquid Phase Reaction Rate Constants", IFI/Plenum Data Co., 1974, p 24. ^b Taken from T. Koenig, "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, 1973, p 129.

are listed some literature data on some representative nonfluorinated diacyl peroxides. The activation enthalpies

(12) J. E. Guillet, T. R. Walker, M. F. Meyer, J. P. Hawk, and E. B. Towne, *Ind. Eng. Chem. Prod. Res. Dev.*, 3, 257 (1964).

(13) D. F. Detar and R. C. Lamb, *J. Am. Chem. Soc.*, 81, 122 (1959).

(14) R. Hiatt in "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley, New York, 1970, p 850.

Table IV. Rate Constants for the Decomposition of the Perfluoro- and Polyfluorodiacyl Peroxides

temp, °C	$10^5 k, s^{-1}$						
	1 ^a	2 ^b	3 ^c	4 ^d	5 ^e	6 ^f	7 ^g
20	2.19 ± 0.04	3.01 ± 0.08		3.29 ± 0.03		4.81 ± 0.08	8.32 ± 0.05
25	4.49 ± 0.07	5.93 ± 0.08	22.6 ± 0.5	6.85 ± 0.03		10.0 ± 0.1	17.3 ± 0.02
30	8.50 ± 0.30	11.1 ± 0.5	42.1 ± 1.0	12.7 ± 0.05	11.4 ± 0.6	19.6 ± 0.2	34.3 ± 0.6
35	17.2 ± 0.4	20.3 ± 0.9	71.7 ± 1.6	25.5 ± 0.2	22.9 ± 0.5	35.2 ± 0.6	68.4 ± 1.7
40	32.6 ± 0.3	42.0 ± 1.2	126 ± 3	50.1 ± 0.6	40.6 ± 1.1	71.6 ± 1.3	134 ± 2
45					80.9 ± 2.1		

^a Initial concentration 0.0299 M. ^b Initial concentration 0.0208 M. ^c Initial concentration 0.0054 M. ^d Initial concentration 0.0212 M. ^e Initial concentration 0.0240 M. ^f Initial concentration 0.0164 M. ^g Initial concentration 0.0273 M.

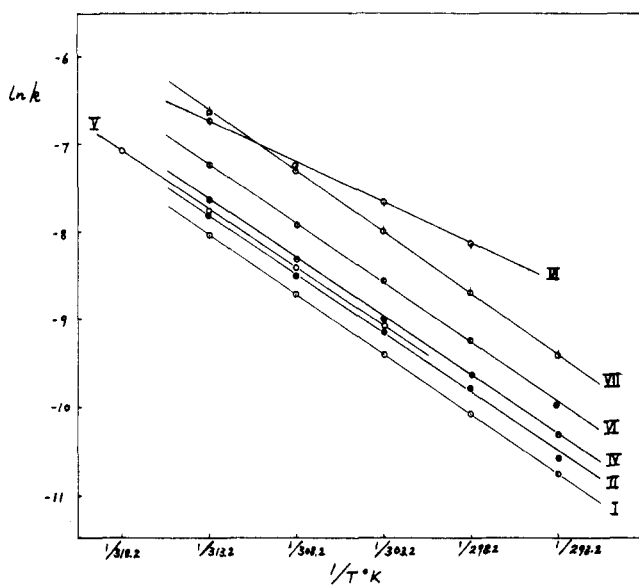


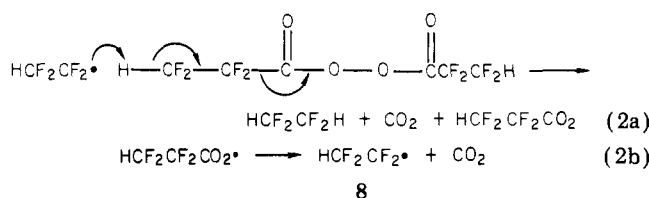
Figure 2. $\ln k$ vs. $1/T$ plots for the thermal decomposition of the perfluoro- and polyfluorodiacyl peroxides.

of six of the fluoro compounds are all around 24 kcal mol⁻¹, some 5 kcal lower than the corresponding hydrocarbon diacyl peroxides. Two possible causes for this fact may be considered. (1) Substitution on the α -carbon by fluorine atoms or perfluoroalkyl groups weakens the peroxidic O—O bond. The α -carbon substituents are two bonds apart from the O—O bond, and the strong polar effects of F or R_F groups can still be felt, while the polar effects of alkyl groups are hardly noticeable.¹⁵ (2) A concerted process involving the simultaneous homolysis of C—C and O—O bonds may be operating. In the hydrocarbon series, a simultaneous lowering of both the ΔH^\ddagger and ΔS^\ddagger values may be considered to be a telling sign of concertion. Comparison of the data in Table II with, e.g., the last two examples of Table III shows an apparent similarity. However, even if concertion could be "proved" in some other way, one would then still face the problem of explaining why these fluorinated groups should stabilize such a transition state, since radicals like CF₃• and R—CF₂• are very reactive radicals.^{16,17} Therefore, further studies are needed to clarify this point.

In the last column of Table II, the rate of decomposition at 30 °C of the perfluorobutyryl compound 1 ($k = 8.5 \times 10^{-5} s^{-1}$) is taken as 1, and the relative rates of other per-

oxides are shown. The rates of 1, 2, and 4–6 are comparable, but those of 3 and 7 are 5-fold and 4-fold faster, respectively. Activation parameters reveal that the accelerations are brought about by different factors. The faster rate of 7 is favored by a larger ΔS^\ddagger value, possibly a manifestation of diminished freedom caused by the crowding of CF₃ groups in the ground-state conformations of these molecules.

The peroxide 3, however, differs from all the others not only in the values of the activation parameters but also in the fact that it undergoes induced decomposition at initial concentrations higher than 0.01 M as shown in Table V. Both peroxides 4 and 5 possess a similar ω -H and peroxide 4 has a shorter chain than peroxide 5. Since peroxide 4 showed no significant signs of undergoing induced decomposition even at much higher concentrations, it is unlikely that peroxide 5 would undergo such a decomposition at lower concentrations. Therefore, the position of the ω -H appears to be crucial to the occurrence of induced decomposition. The following mode of fragmentation with β -scission is implicated in the induced decomposition (eq 2), be it concerted or stepwise, leading



to formation of both tetrafluoroethane and tetrafluoroethylene. However, both of them may be derived also from the disproportionation of radical 8.

Under preparative conditions, a sizable amount (8.7%) of tetrafluoroethane was isolated. Although only a trace of the highly reactive tetrafluoroethylene was detected in the reaction mixture, most of the tetrafluoroethylene formed may have been consumed under the experimental condition where a high radical concentration was maintained from the decomposition of 3 (initial concentration of 3 over 0.36 M). The ΔH^\ddagger and ΔS^\ddagger values for the decomposition of peroxide 3 were determined at a concentration (0.0054 M) at which induced decomposition was insignificant (Table IV). The values show that the ΔS^\ddagger term is unfavorable to the homolysis of 3 relative to other peroxides in this series; it is the lowering of ΔH^\ddagger by 3 kcal which facilitates this process. A possible rationalization of this result is as shown in eq 3.

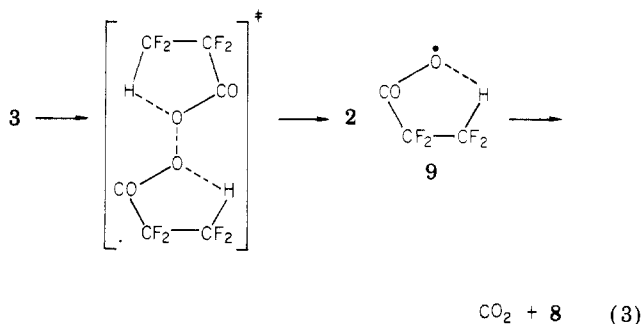
The negative ΔS^\ddagger value indicates that the decomposition of 3 proceeds by a more ordered transition state than that of the other peroxides in this series, as depicted in eq 3. The decomposition may lead to formation of radical 9 stabilized by internal hydrogen bonding. We attribute the lower value of ΔH^\ddagger to this stabilization which is possible only in the decomposition of 3. Since the ω -H of 4 and

(15) M. Szwarc in "Peroxide Reaction Mechanisms", J. O. Edwards, Ed., Wiley, New York, 1962, p 164.

(16) (a) M. Szwarc, see ref 14; (b) R. Hiatt, see ref 13, p 847.

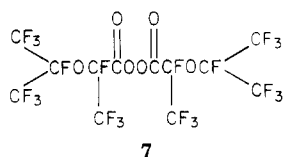
(17) (a) Fluorocarbon Group, *Scientia Sinica*, No.2, 116 (1977); (b) P. D. Bartlett, Q. Rev., *Chem. Soc.*, 24, 473 (1970); *J. Am. Chem. Soc.*, 95, 146, 150 (1973).

(18) T. B. Tripp and R. D. Dunlap, *J. Phys. Chem.*, 66, 635 (1962).

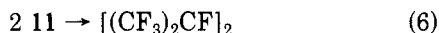
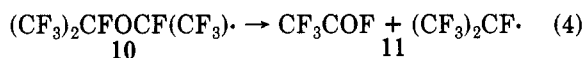


5 are not favorably located for H bonding, ΔH^* values of 4, 5, and 1 are almost identical (Table II).

As shown in Table I, three coupling products are formed in the decomposition of diacyl peroxide 7. This implies

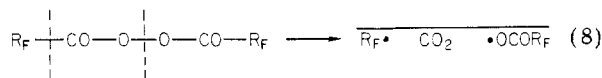


that the perfluoro- α -isopropoxyethyl radicals (10) which are formed by the decarboxylation of perfluoro-2-isopropoxypropionyl radicals may undergo further fragmentation (β scission) and produce the perfluoroisopropyl radical 11:



The coupling reactions occur mostly outside of the solvent cage, since a preliminary test using the scavenger method shows that in the decomposition of 6 only 5% of the coupling products are formed in the cage.

In short, quite a few problems or details remain to be solved for the free-radical decomposition of these fluoro-diacyl peroxides. Among them are (1) whether these processes are stepwise or concerted or both (according to which compound is being referred to), (2) the extent of cage effects in these reactions, (3) the solvent effects, if any, of these reactions, and (4) whether perfluoro esters ($\text{R}_F\text{CO}_2\text{R}_F$) are formed in small amounts. If formed, are they coupling products from stepwise fission, or from a concerted process like eq 8? Further investigations are



planned to study the above problems and other aspects of the chemistry of fluorinated diacyl peroxides. One aspect worthy of mention is that the readily available compound 3 has a half-life of 81 min at 20 °C; it may turn out to be a useful low-temperature initiator for free-radical reactions and polymerizations.

Experimental Section

^{19}F NMR spectra were obtained at 84.6 MHz with a Perkin-Elmer R-32 spectrometer, chemical shifts are expressed as δ values with neat CFCl_3 as an external reference. Mass spectra were obtained on a MAT-112 spectrometer at an ionization energy of 70 eV. GC was conducted on a Shanghai-102 gas chromatograph, with a 3-M column of 30:100 perfluoropolytriazine grease/firebrick 201.

Table V. Rate Constant for the Decomposition of Polyfluorodiacyl Peroxides at Various Concentrations

initial concn, M	Peroxide 3				
	0.00346	0.0054	0.00651	0.0157	0.0249
$10^4 k$ (at 30 °C), $\text{s}^{-1 a}$	4.04	4.21	4.19	5.81	7.49
initial concn, M	Peroxide 4				
	0.00405	0.0101	0.0202	0.0404	
$10^4 k$ (at 30 °C), $\text{s}^{-1 a}$	1.20	1.22	1.23	1.32	

^a The range of experimental uncertainty is $\pm 2.5\%$.

Perfluoroacyl Chlorides.¹⁹ A 1:2 molar ratio mixture of anhydrous perfluorocarboxylic acid and benzoyl chloride (see eq 9) was quickly heated to the boiling point of the carboxylic acid



or slightly above, and the product was cooled by a bath of appropriate temperature. The crude product was carefully fractionated and the purity of the final product examined by GC.

$\text{CF}_3\text{CF}_2\text{CF}_2\text{COCl}$: bp 37 °C (lit.¹⁹ bp 38–39 °C); yield 70%; ^{19}F NMR δ^{20} 84.5 (a, 3 F), 129.8 (b, 2 F), 117.4 (c, 2 F).

$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{COCl}$: bp 128–129 °C [lit.¹⁹ bp 129–130 °C (744 torr)]; yield 77%; ^{19}F NMR δ 84.4 (a, 3 F), 124.4 (b, 4 F), 125.0 (c, 2 F), 125.7 (d, 2 F), 129.5 (e, 2 F), 116.1 (f, 2 F).

$\text{HCF}_2\text{CF}_2\text{COCl}$: bp 32–34 °C; yield 71%; ^{19}F NMR δ 140.0 (a, 2 F, d, $J_{\text{HF}} = 52.4$ Hz), 121.7 (b, 2 F).

$\text{HCF}_2\text{CF}_2\text{CF}_2\text{COCl}$: bp 88 °C (lit.¹⁹ bp 84.5–86.5 °C); yield 70%; ^{19}F NMR δ^{20} 140.9 (a, 2 F, d, $J_{\text{HF}} = 52.4$ Hz), 132.3 (b, 2 F), 126.1 (c, 2 F), 116.3 (d, 2 F).

$\text{HCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{COCl}$: bp 126–128 °C; ^{19}F NMR δ 141.3 (a, 2 F, d, $J_{\text{HF}} = 52.2$ Hz), 132.8 (b, 2 F), 126.6 (c, 2 F), 124.4 (d, 4 F), 116.2 (e, 2 F).

Perfluoro-2-n-propoxypropionyl Fluoride.²¹ Perfluoro-propylene oxide was passed into a 0.3-L stainless-steel reactor containing anhydrous KF dissolved in diglyme, and the dimeric product $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COF}$ was obtained in 53% yield. The crude product was fractionated; bp 55.5–56.0 °C.

$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{COF}$: ^{19}F NMR δ^{22} 85.6 (a, 3 F), 134.2 (b, 2 F), 86.8 (c, 2 F, q, $J_{\text{FF}} = 152.3$ Hz), 134.6 (d, 1 F), 86.3 (e, 3 F), -21.7 (f, 1 F).

Perfluoro-2-isopropoxypropionyl Fluoride.²³ In addition to anhydrous KF and diglyme, hexafluoroacetone was placed in the above-mentioned reactor and propylene oxide passed into it. The 1:1 addition product $(\text{CF}_3)_2\text{CFOCF}(\text{CF}_3)\text{COF}$ was obtained in 61% yield. Fractionated product boiled at 54 °C.

$(\text{CF}_3)_2\text{CFOCF}(\text{CF}_3)\text{COF}$: ^{19}F NMR δ (83.4, 84.6 (a, 6 F), 148.1 (b, 1 F), 130.3 (c, 1 F), 86.1 (d, 3 F), -22.5 (e, 1 F).

Fluorinated Diacyl Peroxides. Definite volumes of Freon-113 were placed in a reactor kept at -5 to -7 °C and stirred. On the basis of the molar ratio of $\text{R}_F\text{COX}/\text{NaOH}/\text{H}_2\text{O}_2$ (1:1:0.5), exact amounts of aqueous NaOH (0.12 g of NaOH/mL) were added, followed by 30% aqueous H_2O_2 . After the mixture was stirred rapidly, an accurate amount of precooled acyl halide was added. Two minutes of stirring was followed by several minutes of stirring at a slightly higher temperature (~ 0 °C). The lower organic layer was washed successively by ice-cooled saturated aqueous NaHCO_3 and water. The yield or the concentration of the product was

(19) A. M. Lovelace, et al., "Aliphatic Fluorine Compounds", Reinhold, New York, 1958, p 212.

(20) J. W. Emsley, et al., Eds. *Prog. Nucl. Magn. Reson. Spectrosc.*, 7, 142, 146, 175 (1971).

(21) U. S. Patent, 3 322 826 (1967); *Chem. Abstr.*, 67, 44292 (1967).

(22) J. T. Hill, *J. Macromol. Sci., Chem.*, A8, 499–500 (1974).

(23) S. Selman, U.S. Patent, 3 274 239; *Chem. Abstr.*, 65, 20029a (1966).

Table VI. Scavenger Experiment Results of the Decomposition of 6

[CCl ₃ Br], M	0.0033	0.013	0.20	0.26	0.33	0.11	2.5
fraction of scavenged	0.14	0.49	0.58	0.71	0.95	0.95	0.96

determined by iodometry. The Freon solution was dried over anhydrous Na₂SO₄ and preserved at -78 °C.

Kinetic Measurements. The above-mentioned dilute Freon solutions (≤0.02 M) were sealed in glass tubes under high-purity N₂. A whole set of these tubes was placed in a thermostat (±0.05 °C), and they were taken out at specified times and immediately frozen to dry ice temperature. The tubes were opened while cool, and the undecomposed peroxide titrated by standard iodometry.²⁴

First-order rate constants at different temperatures and activation parameters were calculated by linear regression analysis. Values of rate constants and the standard deviations of determination are shown in Table IV. Results of the preliminary tests of rate-concentration relationships upon which the proper initial concentrations for kinetic determinations were chosen are given in Table V.

Decomposition Products of Diacyl Peroxides. The above-mentioned Freon-113 solutions (5-10 mL) of diacyl peroxides (0.14-0.56 M) were kept at room temperature for 2 days to allow complete decomposition; the resulting reaction mixtures were analyzed by GC. The main products, which in all cases corresponded to the coupling products of perfluoroalkyl radicals, were separated by preparative GC and identified by NMR and mass spectra. Yields of the coupling products are shown in Table II; they were determined by GC with the pure separated samples as calibration standards. Minor products (all below 5%) have not been identified, but from the information obtained by GC/MS, they appear to be products from halogen abstraction by perfluoroalkyl radicals.

(CF^a₃CF^b₂CF^c)₂: ¹⁹F NMR δ 75.1 (a, 3 F), 116.6 (b, 2 F), 120.3 (c, 2 F); MS *m/e* 319 [(M - F)⁺], 269, 231, 219, 200, 181, 169, 150, 131, 119, 100, 69.

(CF^a₃CF^b₂CF^c₂CF^d₂CF^e₂CF^d₂CF^d₂)₂: ¹⁹F NMR δ 81.9 (a, 3 F), 123.0 (b, 2 F), 124.0 (c, 2 F), 127.4 (d, 8 F).

(HCF^a₂CF^b)₂: ¹⁹F NMR δ 142.0 (a, 2 F, d, *J*_{HF} = 54.0 Hz), 135.1 (b, 2 F); MS *m/e* 151 [(M - CF₂H)⁺], 132, 113, 101, 82, 69, 51.

HCF^a₂CF^b₂CF^c₂CF^d)₂: ¹⁹F NMR δ 146.3 (a, 2 F, d, *J*_{HF} = 52.4 Hz), 133.3 (b, 2 F), 126.6 (c, 2 F), 125.2 (d, 2 F); MS *m/e* 332 [(M

- CF₃H)⁺], 313, 295, 281, 263, 251, 243, 231, 220, 213, 201, 181, 169, 163, 151, 131, 119, 101, 100.

(HCF^a₂CF^b₂CF^c₂CF^d₂CF^e₂CF^d)₂: ¹⁹F NMR δ 141.3 (a, 2 F, *J*_{HF} = 52.2 Hz), 133.4 (b, 2 F), 127.0 (c, 2 F), 125.3 (d, 6 F).

(CF^a₃CF^b₂CF^c₂OCF^d(CF^e₃)₂)₂: ¹⁹F NMR δ 85.2 (a, 3 F), 134.2 (b, 2 F), 84.0 (c, 2 F), 143.3, 146.2, (d, 1 F), 80.3, 82.0 (e, 3 F); MS *m/e* 385 [(M - C₃F₇O)⁺], 297, 285, 263, 219, 200, 197, 169, 150, 147, 131, 119, 100, 97, 69.

[(CF^a₃)₂CF^bOCF^c(CF^d₃)₂]: ¹⁹F NMR δ 82.7, 84.0 (a, 3 F), 143.8 (b, 1 F), 136.0, 136.8 (c, 1 F), 79.7, 80.9 (d, 3 F); MS *m/e* 551 [(M - F)⁺], 501, 385, 363, 335, 313, 297, 285, 219, 200, 197, 169, 150, 147, 131, 119, 100, 97, 69.

(CF^a₃)₂CF^bCF^c(CF^d₃)OCF^e(CF^f₃)₂: ¹⁹F NMR δ 74.9 (a, 6 F), 186.6 (b, 1 F), 143.9 (c, 1 F), 79.9 (d, 3 F), 131.2 (e, 1 F), 83.2, 84.3 (f, 6 F); MS *m/e* 435 [(M - F)⁺], 385, 297, 285, 269, 247, 235, 219, 200, 197, 181, 161, 132, 119, 97.

[(CF^a₃)₂CF^b]₂: ¹⁹F NMR δ²⁵ 74.7 (a, 6 F), 183.8 (b, 1 F); MS *m/e* 319 [(M - F)⁺], 250, 162, 150, 132, 124, 112, 74, 62.

Scavenger Experiment. The decomposition of peroxide 6 in 0.2 M Freon-113 solution was carried out at room temperature with the addition of various amounts of a scavenger, CCl₃Br. After the decomposition was completed, the amounts of the coupling products were determined by GC. The yields of coupling products diminish with the increase of the relative concentration of CCl₃Br and approach a constant value which corresponds to ~5% of the coupling products obtained without the addition of CCl₃Br. Typical results are shown in Table VI Scavenged product, CF₃-CF₂-CF₂-OCF(CF₃)Br, was isolated and identified.

CF^a₃CF^b₂CF^c₂OCF^d(CF^e₃)Br: ¹⁹F NMR δ 85.7 (a, 3 F), 133.8 (b, 2 F), 88.8 (c, 2 F, AB q, Δδ = 3.6 ppm, *J*_{AB} = 145 Hz), 80.8 (d, 1 F), 89.3 (e, 3 F).

Registry No. 1, 336-64-1; 2, 34434-27-0; 3, 21934-53-2; 4, 308-35-0; 5, 32687-76-6; 6, 56347-79-6; 7, 72836-49-8; *n*-C₃F₇COCl, 375-16-6; *n*-C₇F₁₅COCl, 335-64-8; HCF₂CF₂COCl, 663-73-0; H(CF₂)₄COCl, 376-71-6; H(CF₂)₆COCl, 41405-35-0; *n*-C₃F₇OCF(CF₃)COF, 2062-98-8; *i*-C₃F₇OCF(CF₃)COF, 10372-97-1; (*n*-C₃F₇)₂, 355-42-0; (*n*-C₇F₁₅)₂, 307-62-0; (HCF₂CF₂)₂, 377-36-6; [H(CF₂)₄]₂, 307-99-3; [H(CF₂)₆]₂, 865-84-9; [*n*-C₃F₇OCF(CF₃)]₂, 2501-01-1; [*i*-C₃F₇OCF(CF₃)]₂, 81219-02-5; *i*-C₃F₇OCF(CF₃)CF(CF₃)₂, 81219-03-6; (*i*-C₃F₇)₂, 354-96-1; CF₃CF₂CF₂OCF(CF₃)Br, 81219-04-7; perfluorobutanoic acid, 375-22-4; perfluorooctanoic acid, 335-67-1; 2,2,3,3-tetrafluoropropanoic acid, 756-09-2; 2,2,3,3,4,4,5,5,5-octafluoropentanoic acid, 376-72-7; 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanoic acid, 1546-95-8; perfluoropropylene oxide, 428-59-1; hexafluoroacetone, 684-16-2.

(24) C. D. Wagner, *Anal. Chem.*, **19**, 976 (1947); P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954).

(25) R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Am. Chem. Soc.*, **82**, 5831 (1960).

Oxidation of Some 2-Methoxyphenols with Chlorous Acid

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Oxidation of 3-ethoxy-4-hydroxy-, 4-hydroxy-3-methoxy-5-methyl-, 3-chloro-4-hydroxy-5-methoxy-, and 2-hydroxy-3-methoxybenzaldehyde with chlorous acid gives, by oxidative aromatic ring cleavage between the oxygen-bearing carbon atoms, derivatives of (2*Z*,4*Z*)-2,4-hexadienedioic acid in low yields. Chlorous acid oxidation of 2-methoxyphenol and 3-hydroxy-4-methoxybenzaldehyde yields methoxy-1,4-benzoquinone and 5,5-dichloro-6,6-dihydroxy-2-methoxy-2-cyclohexene-1,4-dione, respectively. The hydrate as well as the corresponding methyl hemiacetal undergoes base-catalyzed ring contraction to a derivative of 1-hydroxy-4-oxo-2-cyclopentenecarboxylic acid. The kinetics of the ring contraction of the hydrate was investigated in aqueous solutions in the pH range 1.15-3.65, where the rearrangement appears to be subject to specific base catalysis.

Oxidative intradiol ring cleavage of 1,2-diphenols with formation of 2,4-hexadienedioic (muconic) acids is an important process in degradation of aromatic compounds by aerobic microorganisms.² Notably, the process plays a

significant role in soil degradation of plant-produced phenolics, being thus a part of the carbon cycle of the

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